

# Influence of reactant concentration on nano crystalline PbS thin films prepared by Chemical Spray Pyrolysis

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Nanocrystalline PbS thin films were prepared by simple and cost effective chemical spray pyrolysis (CSP) technique. Lead acetate and Thiourea were used as a source of Pb and S respectively. The structural and optical properties of the PbS films were studied. Structural cubic phases of the PbS thin films were identified by X-ray diffraction with preferential orientation along (200) plane. The average grain size of the film is calculated using Scherer's relation and it is in the order of nanometers. The optical properties of the films were studied by measuring their optical Absorbance and transmittance as a function of wavelength. UV-VIS spectrum of the film showed that the optical band gap decreases with increase in the molarities of precursor solution. The surface morphological studies of the films were analyzed by scanning electron microscope.

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## 1. Introduction

Lead sulfide (PbS) have been widely studied because of their novel properties and wide range of applications. It is direct narrow gap semiconductor material with the band gap energy of 0.4 eV at 300 K and Bohr radius of 18 nm [1-4]. So lead sulfide thin films have been used as photothermal conversion applications [5,6], IR detectors [7,8], sensors [9], and decorative and solar cell application [10,11] etc.,

Thin films of Lead sulfide can be prepared by number of methods which includes chemical bath deposition[12], micro wave heating [13], electro deposition [14] etc., Among many methods available the spray pyrolysis technique is one of the simplest method for producing PbS thin films [15,16]. The aim of this work is to study the influence of precursor concentration on the structural, optical and surface morphological characteristics of PbS thin films prepared at 220 °C.

## 2. Experimental

The PbS thin films were grown on ordinary glass slides (7.5 cm × 2.5 cm). The precursor solution of Lead sulfide thin films was obtained by dissolving the salts of lead acetate ((Pb (C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>.3H<sub>2</sub>O) and thiourea (CH<sub>4</sub>N<sub>2</sub>S) in the molar ratio of 0.005M: 0.005M in double distilled water. The amount of solution was made together 50 ml. The aqueous solution was then sprayed on the preheated glass substrate maintained at 220 °C. Compressed dry air at a pressure of 12 kg/cm<sup>2</sup> from an air compressor via an air filter cum regulator was used as the carrier gas. The spray rate of the solution was maintained at 3 ml/min. The

distance between the spray nozzle and the substrate is 35 cm. Total time is 45 minute for all deposition.

Film obtained due to endothermic thermal decomposition that takes place at the hot surface of the substrate. By increasing the molarity of lead acetate and thiourea to 0.01M: 0.01M in the precursor solution another set of PbS thin films were deposited without changing the other process parameter. Lead Sulfide films obtained from .005M and .01M of precursor is named as sample (a) and sample (b) respectively.

The thickness of the films was measured by micro weighing technique. The thickness of the sample (a) and sample (b) found to be 1.6 μm and 2.2 μm. The structural study was determined by X-ray diffractometer (Rigaku Model RAD II A) with CuKα radiation (α-1.541 Å). The data were recorded at a scan rate of 0.2°/min and in the range of 20°<2θ<80°.

The surface morphologies of the films were determined by using Scanning Electron Microscope (JEOL 1600). Prior to imaging, the films were sputtered with thin gold film to enhance the emission of secondary electron for better imaging.

Optical transmittance and band gap energy was measured by UV-VIS single beam spectrophotometer (ELICO-159) with uncoated glass as reference. The experimental accuracy for absorbance is ±0.005 abs and of wavelength is ± 0.05 nm.

## 3. Results and discussion

### 3.1. Structural studies

Fig. 1 shows the X-ray diffraction pattern of as deposited PbS with different concentration of the

precursor [sample (a) and sample (b)]. Observation of the films shows the smooth surface and highly adhesive nature of the film with glass substrate. The XRD pattern of PbS films prepared with lower concentration at 220 °C is found to have a better polycrystalline nature oriented along the (111), (200), (220) and (311) planes at  $2\theta = 25.86^\circ$ ,  $29.98^\circ$ ,  $43.27^\circ$  and  $51.24^\circ$  respectively. As the concentration of the precursor increases there is an increase in intensity of (200) plane as well as some additional peaks were also observed along with the standard peaks. The other peaks observed with lower intensity are (222), (400) and (420). This may be due to the increase in atomic density in the planes attributed to higher concentration of the precursor and thickness. No other impurities peaks are observed. Also the intense peak (200) oriented along lattice plane indicates that the growth of the grain is parallel to the substrate. All peaks can be indexed to cubic PbS phase as compared with standard JCPDS card No.78-1901. X-ray line broadening technique (XDLB) was used to estimate the grain size of the film by using Scherer's formula [17, 18]

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

Where D is the grain size,  $\theta$  is the diffraction angle, K is the shape factor (0.89),  $\lambda$  is the wavelength of x-ray and  $\beta$  is full width and half maximum (FWHM) of intense peak. The grain size of PbS thin film is calculated by using Scherer's formula is found to be 29 nm and 35 nm for sample (a) and sample (b) respectively. This small grain size of the film is reveals that the nanocrystalline nature of the film. The d-spacing is calculated for cubic system using the formula,

$$d = a / \sqrt{h^2 + k^2 + l^2} \quad (2)$$

A comparison of the calculated d-values and the standard JCPDS value (78-1901) is given in Table 1.

Table 1. Comparison of XRD data with JCPDS.

d-spacing(Sample b)		
(h k l) plane	Calculated	Standard (78-1901)
(111)	3.4376	3.4245
(200)	2.9668	2.9657
(220)	2.0926	2.0971
(311)	1.7894	1.7884
(222)	1.7115	1.7122
(400)	1.4849	1.4828
(420)	1.3233	1.3263

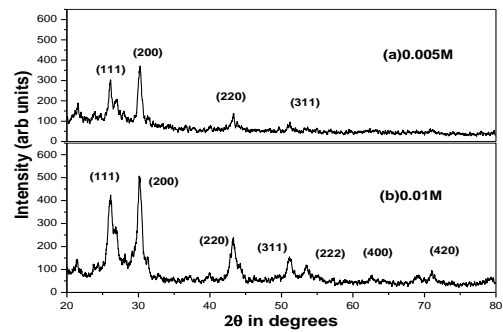


Fig. 1. XRD patterns of PbS thin films.

### 3.2. Optical studies

The absorption spectra of PbS thin film samples (a) and (b) prepared at 220 °C on glass substrate were recorded as a function of wavelength range 400 nm-1000 nm with glass as reference is shown in Fig. 2. It shows that absorbance of the both the samples decreases with increase in wavelength. As the concentration of the precursor increases from 0.005 to 0.01 there is a drastic increase in absorbance. It is attributed to larger thickness of the film at higher concentration due to which more states will be available for the photons to be absorbed [19]. Transmittance spectra of PbS samples as a function of wavelength is shown in Fig. 3. Here the film deposited with lower concentration shows higher transmittance and this makes it good material for optical coatings. The decrease in transmittance with increase in concentration may be due to increasing absorption. The absorption coefficient ( $\alpha$ ) is calculated using Lambert's law [20],

$$\alpha = 2.303A / t \quad (3)$$

Where 'A' is the absorbance and 't' is the film thickness. Fig. 4 shows the absorption coefficient spectra of PbS thin films as a function of wavelength in the range of 400 nm - 1000 nm. It shows that as the concentration increase the absorption coefficient is also increases.  $\alpha$  is calculated for both the film and it is found to be in the order of  $10^6 \text{ cm}^{-1}$ .

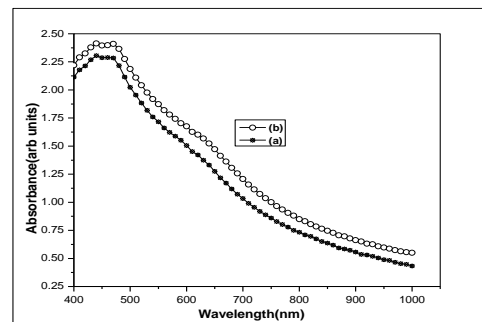


Fig. 2. Absorbance spectra of PbS thin films.

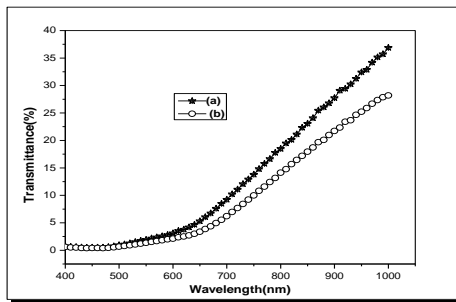


Fig. 3. Transmittance spectra of PbS thin films.

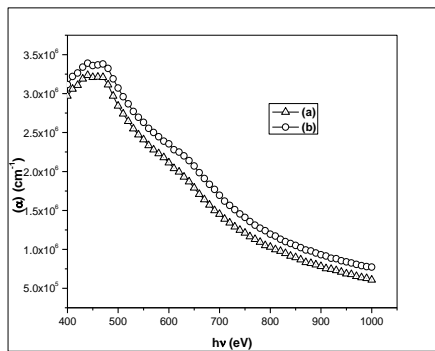


Fig. 4.  $\alpha$  Vs  $h\nu$  of PbS thin films.

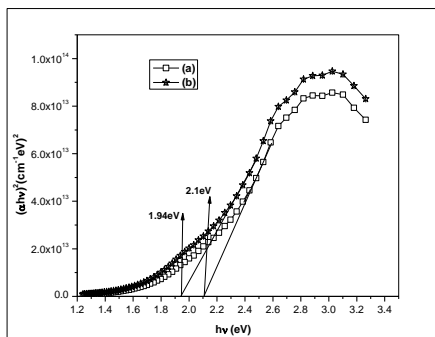


Fig. 5. Tauc's plot of PbS thin films.

The maximum value of  $\alpha$  of the film was in the visible region with an average value of  $3.25 \times 10^6 \text{ cm}^{-1}$  and the minimum value was at 1000 nm near infrared region. It is attributed increase the crystallinity of the film at higher concentration [21].

The optical band gap  $E_g$  was calculated using Tauc's plot  $(\alpha h\nu)^2$  Vs  $h\nu$  and it shows in Fig. 5. It is observed that the increase in concentration of precursor in PbS thin film yields a slight decrease in band gap from 2.1 eV to 1.94 eV. The shrinkage may be due to Moss –Brustien shift.

### 3.3. SEM studies

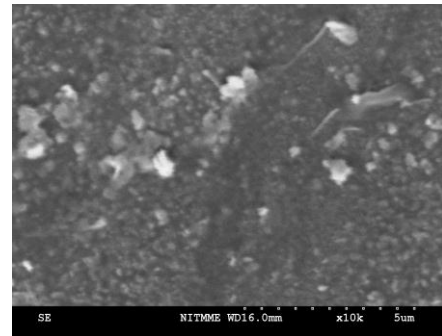


Fig. 6. SE image of sample (0.005M).

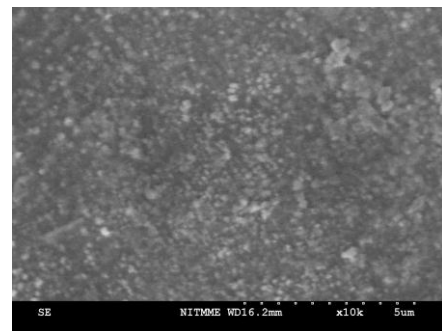


Fig. 7. SE image of sample (0.01M).

Figs. 6 and 7 shows the SE micrograph of PbS thin films of 0.005 and 0.01M. Initially, the film growth is poor, and non uniform whereas as at higher concentration the film shows homogeneous and uniform surface covered with grains. It confirms as the concentration increases there is a clear improvement in crystalline which agrees with Scherer's results.

### 4. Conclusions

PbS thin films (1.6 and 2.2  $\mu\text{m}$  thickness) deposited by simple chemical spray technique. The influence of reactant concentration on the structural, optical and morphology of the film was studied. X-ray diffraction study reveals that the film has preferential orientation along the plane (200). PbS films deposited with higher concentration of precursor shows clear improvement in crystallinity. Lattice d spacing and crystallite size of the films were calculated.

The optical studies show that there is an increase in absorbance with thickness and concentration. The band gap energy was found to be 1.94 eV with direct transition. The surface morphology of the films reveals that grain size depends on the concentration of the precursor.

## References

- [1] S. Seghaier, N. Kamoun, R. Brini, A. B. Amara *Materials Chemistry and Physics* **97**, 71 (2006).
- [2] Rakesh K. Joshi, Sathish Mohan, S. K. Agarwal, H. K. Seghal. *Thin solid films* **80** (2004).
- [3] Sushil Kumar, T. P. Sharma, M. Zulfequar, M. Husain *Phy B: Condensed Matter* **325**, 8 (2003).
- [4] Titipun Thongtem, Sulawan Kaowphong and Somchal Thongtem, *Ceramics International* (2007).
- [5] O. P. Agnihotri, B. K. Gupta, *Solar selective surfaces*, Wiley, New York, 130 (1981).
- [6] T. J. Mc. Mahan, S. N. Jaspersen, *Applied Optics*, **13**(12), 2750 (1974).
- [7] T. K. Chaudhuri, Ph. D. Thesis, Indian Institute of Technology, Kharagpur, India (1984).
- [8] T. S. Moss, *Proc. Institute of Radio Electronics, IRE* **43**, 1869 (1955)
- [9] H. Hirata, K. Higashiyama, *Bull. Chem. Soc. Jpn.* **44**, 2420 (1971).
- [10] P. K. Nair, V. M. Garcia, A. B. Hernandez, M. T. S. Nair, *J. Phys. D: Apply. Phys.* **24**, 1466 (1991).
- [11] Ileana Pop, Cristina Nascu, Violeta Ionesu, E. Indvea, I. Bratu, *Thin Solid Films*, **307**, 240 (1997).
- [12] Yonghong Ni, Jianming Hong, Xiang Ma, Zheng Xu, *Cryst.Growth*, **262**, 399 (2004).
- [13] S. Seghaier, N. Kamoun, R. Brini, A. B. Amara, *Materials Chemistry and Physics* **97**, 71 (2006).
- [14] Maheshwar Sharon, K. S. Ramaiah, Mukul Kumar, M. Neumann-spallart, C. Levy-Clement, *Electro anal. Chem.* **436**, 49 (1997).
- [15] B. Thangaraju, P. Kaliannan, *Semicond. Sci. Technology*, **15**, 849 (2000).
- [16] E. Elshafie, M. M. Elzaidia, H. H. Afify, M. H. Khalil, *Proc.2<sup>nd</sup> Saudi Sci. Conf. Fac. Sci. KAU*, 15-17, PART II, 251 (2004).
- [17] L. G. Berry (Ed.) *ASTM Powder Diffraction File, Sets 1 to 5, Inorganic, Vol.PDIS-5LRB*, (1967).
- [18] W. L. Bragg, *Proc. Camb Phil. Soc.*, **17**, 43 (1912).
- [19] M. Y. Nadeem, Waqas Ahmed, *Turkey Journal of Physics*, 24-651, (2000).
- [20] F. Hoffmann, P. Mayr, A. Mehner, H. Klumper-Westkamp, *Thin Solid Films*, **308-309**, 365 (1997).
- [21] A. F. Gibson, *Proc. Phys. Soc. London*, **B63**, 756 (1950).

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